

2018-05

# Mobilisation kinetics of hazardous elements in marine plastics subject to an avian physiologically-based extraction test.

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<http://hdl.handle.net/10026.1/11184>

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10.1016/j.envpol.2018.01.023

Environ Pollut

Elsevier BV

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3 **Mobilisation kinetics of hazardous elements in marine**  
4 **plastics subject to an avian physiologically-based**  
5 **extraction test**

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21 Accepted 9 January 2018

22 Available online 16 February 2018

23 <https://doi.org/10.1016/j.envpol.2018.01.023>

24 Under embargo until 9 January 2019  
25  
26

## Abstract

Samples of plastic collected from two beaches in southwest England ( $n = 185$ ) have been analysed by XRF spectrometry for elements that are hazardous or restricted in synthetic polymers (namely, As, Ba, Br, Cd, Cr, Hg, Pb, Sb and Se). Overall, one or more restricted element was detected in 151 samples, with 15 cases exhibiting non-compliance with respect to the Restriction of Hazardous Substances (RoHS) Directive. Twelve plastics that were RoHS-non-compliant were subsequently processed into microplastic-sized fragments and subjected to an avian physiologically-based extraction test (PBET) that simulates the chemical conditions in the gizzard-proventriculus of the northern fulmar. Kinetic profiles of metal and metalloid mobilization in the PBET were fitted using a pseudo-first-order diffusion model with rate constants ranging from  $\sim 0.02$  to  $0.5 \text{ h}^{-1}$ , while profiles for Br were better fitted with a parabolic diffusion model and rate constants of  $7.4$  to  $9.5 (\mu\text{g L}^{-1})^{-1} \text{ h}^{-1}$ . Bioaccessibilities, based on maximum or equilibrium concentrations mobilized relative to total (XRF) concentrations, ranged from  $< 1 \%$  for Cd and Se in polyethylene and polypropylene to over  $10\%$  for Br in a sample of expanded polystyrene and Pb in a sample of PVC. Calculations suggest that ingested plastic could contribute about  $6\%$  and  $30\%$  of a seabird's exposure to and accumulation of Pb and brominated compounds, respectively.

**Capsule:** The kinetics of mobilisation and measures of bioaccessibility have been determined for hazardous elements in marine plastics using an avian digestive extract

**Keywords:** microplastics; heavy metals; brominated flame retardants; avian bioaccessibility; mobilization kinetics

## 1. Introduction

Because of their relatively low manufacturing costs, versatility, imperviousness to water and low density, plastics have a wide variety of applications in the packaging, storage, plumbing, construction, medical, furniture, electronic, agriculture, transportation and maritime sectors. Although many thermoplastics can be readily recycled, there are environmental issues associated with plastic use and consumption that have been well-publicised over the past few decades, including energy requirements for their production from crude oil, emissions associated with disposal by landfill or incineration, littering and marine pollution. Regarding the latter, floating, deposited and beached plastics pose risks to marine wildlife, and in particular to procellariiform seabirds through entanglement and ingestion (Phillips et al., 2010; Wilcox et al., 2015). The inadvertent or incidental consumption of indigestible plastics by birds feeding or foraging may result in starvation, damage to the digestive tract and reduced growth. Moreover, if plastics are associated with toxic chemicals, these have the potential to undergo mobilisation under the acidic conditions of the gizzard and subsequent absorption in the higher pH environment of the small intestine.

With respect to hydrophobic organic pollutants that have adsorbed to the surface of plastics from sea water, it is unclear whether ingestion provides a significant vector for their bioaccumulation since model calculations suggest an overwhelming contribution to body burden from the diet (Herkze et al., 2016). However, empirical studies have revealed that organic chemicals present in plastics as functional additives and occurring at concentrations many orders of magnitude higher than adsorbed pollutants are often readily mobilised in the simulated digestive juices of

procellariiforms (Tanaka et al., 2015). Regarding inorganic chemicals, compounds of hazardous metals and metalloids were often added to historical plastics at percentage concentrations as fillers, pigments, stabilisers and flame retardants (Hansen et al., 2013), while substantial quantities of residual catalysts and intermediates may also be present if such materials had been expanded or extruded (Turner and Lau, 2016). Accordingly, older marine plastics are often characterised by the presence of chemicals like lead chromate, cadmium sulphoselenide and antimony-based synergists, many of which have since been restricted or phased out (Turner, 2016).

In a recent article, a limited number of individual, beached microplastics (< 5 mm) containing one or more hazardous elements were subjected to an avian physiologically-based extraction test (PBET) (Massos and Turner, 2017). Although mobilisation of small but significant quantities of Cd and Pb was evident, an evaluation of the mechanisms and kinetics of dissolution was thwarted by concentrations that were close to control levels or instrumental detection limits. In the present study, such constraints are circumvented by undertaking PBETs on larger and controlled quantities of microplastics that have been prepared from primary and secondary macroplastics in order to assess the potential for hazardous element exposure to sea birds. The samples for study were retrieved from local beaches and selected on the basis of non-compliance according to the Restriction of Hazardous Substances Directive on electronic plastics (RoHS, 2006); that is, in a homogeneous material of any new or recycled product, concentration limits are 100  $\mu\text{g g}^{-1}$  for Cd, 1000  $\mu\text{g g}^{-1}$  for Cr(VI), Hg and Pb, and 1000  $\mu\text{g g}^{-1}$  for specific brominated flame retardants and where total Br is a commonly employed proxy (Guzzonato et al., 2016). Additional, potentially hazardous elements were also considered that are

commonly co-associated with RoHS-elements and that have restrictions on migration from plastics according to the original European toy safety standard, EN 71-3:1994 (Cordeiro et al., 2012); namely: As, Ba, Se and Sb.

## **2. Materials and methods**

### *2.1. Sampling and sample processing*

Samples of plastic were collected from two sand-gravel beaches in Plymouth Sound, south west England (Firestone Bay: 50.36054, -4.16252; and Mount Batten: 50.35771, -4.12755). Distinctive objects and fragments of plastic and pieces of expanded or extruded polymer of between about 5 and 250 mm in length, but excluding food packaging that had been discarded in situ, were retrieved after high water from the most recent strandline using plastic tweezers and transferred to a polyethylene storage box. In the laboratory, samples were rinsed in Millipore Milli-Q water through a 2-mm sieve and with the aid of a Nylon brush in order to remove debris and silt before being dried at 40°C for 24 hours.

### *2.2. XRF analysis*

Samples were analysed by energy-dispersive field-portable-XRF for a suite of elements, of which those that are restricted in plastics according to the RoHS Directive or EN71 Standard are the focus of the present study (i.e. As, Ba, Br, Cd, Cr, Hg, Pb, Sb, Se). Thus, in the laboratory, a battery-powered Niton XRF analyser (model XL3t 950 He GOLDD+) was fixed, nose-upwards, into a Thermo Fisher Scientific accessory test stand (PN 420-017) and connected to a laptop computer via USB and operated under conditions detailed elsewhere (Turner and Solman, 2016). Samples were measured for thickness through the flattest (measurement) surface

using digital callipers before being placed on a 20 cm<sup>2</sup>, 3.6 µm thick polyester film that was suspended above the detector window. With the shield of the stand closed, measurements in a low density ‘plastics’ mode and with appropriate thickness correction were activated through the laptop for 60 seconds, comprising an initial scan for Cl to discriminate polyvinyl chloride- (PVC-) and non-PVC-based plastics, and subsequent periods of counting of 40 seconds at 50 kV and 40 µA and 20 seconds at 20 kV and 100 µA. Spectra were quantified by fundamental parameters to yield elemental concentrations on a dry weight basis (in µg g<sup>-1</sup>) and a counting error of 2σ (95% confidence) that were downloaded to the laptop using Niton data transfer (NDT) PC software. False positives for As in the presence of Pb (resulting from spectral overlap of As-Kα = 10.54 keV and Pb-Lα = 10.55 keV) were eliminated on examination of individual spectra displayed by the NDT software.

For quality assurance purposes, two Niton polyethylene discs that had been impregnated with various elements were analysed at regular intervals throughout each measurement session. Specifically, disc 1 (PN 180-554, batch SN PE-071-N) contains Br, Cd, Cr, Hg and Pb at or close to their respective RoHS limits, while disc 2 (PN 180-619, LOT#T-18) contains all elements listed in the original toy safety standard at concentrations ranging from about 50 µg g<sup>-1</sup> (As) to 700 µg g<sup>-1</sup> (Ba). Measured versus certified concentrations resulting from all analyses of both discs and shown in Figure 1 reveal agreement within 10% in all cases with the exception of Br in disc 1 and Hg in disc 2 (agreement within 12%). Also shown in Figure 1 are indicative measurement limits of detection for each element, based on mean counting errors derived from all disc analyses multiplied by 1.5 (i.e. 3σ).

### 2.3. FTIR analysis

The composition of samples for the extraction tests, selected on the basis of RoHS-non-compliance and as described below, were determined by Fourier transform infrared (FTIR) spectroscopy using a Bruker ALPHA Platinum attenuated total reflection QuickSnap A220/D-01 spectrometer. Sample offcuts of about 20 mg were clamped down on to the ATR diamond crystal before measurements, consisting of 16 scans in the range 4000 to 400  $\text{cm}^{-1}$  and at a resolution of 4  $\text{cm}^{-1}$ , were activated via Bruker OPUS spectroscopic software. Identification involved a comparison of sample transmittance spectra with libraries of reference spectra.

### 2.4. PBET

The avian extraction test was modelled on the digestive characteristics of the proventriculus-gizzard of the northern fulmar, *Fulmarus glacialis*, a procellariiform known to ingest substantial quantities of microplastics and an OSPAR indicator species of plastic pollution (OSPAR, 2008; Avery-Gomm et al., 2012). Samples were first manually processed to a size of < 3 mm using a stainless steel grater or scalpel before ~100 mg portions were accurately weighed into individual 60 ml screw-capped polypropylene centrifuge tubes. Forty ml of a digestive fluid, comprising 1% pepsin (lyophilised powder from porcine gastric mucosa; Sigma-Aldrich) in 0.1 M NaCl solution whose pH had been adjusted to 2.5 by addition of 1 M HCl, was then added to each tube, including three without solids and which served as controls. Tubes were subsequently capped and the contents incubated in a shaking water bath set at 100 rpm and 40 °C. After time intervals of about 1, 2, 5, 15, 25 and 160 h, and taking care not to abstract plastic fragments, 1-ml aliquots of extract from each tube were pipetted



into individual Sterilin tubes where they were diluted to 5 ml with 2% HNO<sub>3</sub> and stored at 4 °C and in the dark pending analysis.

### *2.5. Extract analysis*

PBET extracts were analysed in triplicate for the restricted elements considered by collision cell-ICP-MS using a Thermo X-series II (Thermo Elemental, Winsford UK) with a concentric glass nebuliser and conical spray chamber. The ICP was calibrated externally using five mixed standards and five blanks prepared in 2% HNO<sub>3</sub> and operated under conditions described elsewhere (Turner and Holmes, 2015). Limits of detection, based on three standard deviations arising from blank measurements, ranged from about 0.5 µg L<sup>-1</sup> for Cd, Pb and Se to about 10 µg L<sup>-1</sup> for Br.

## **3. Results and Discussion**

### *3.1. Sample characteristics*

A total of 185 samples of primary and secondary plastics were analysed by XRF, and a summary of the concentrations of hazardous and restricted elements is given in Table 1. Detection frequency ranged from about 2% for Se to over 40% for Ba and Cr, and overall, one or more element was detected in 151 cases. Non-detection was usually associated with distinct objects (e.g. bottle lids, toys, straws) while the highest concentrations of one or more restricted elements were generally encountered in both primary and secondary plastics that were either brightly coloured and/or of PVC-construction, and in neutrally- or brightly-coloured pieces of expanded plastic. Non-compliance according to RoHS criteria (RoHS, 2006) was observed in 12 samples based on Cd or Pb concentrations, with potential non-compliance occurring in three additional samples based on total Br concentrations in excess of 1000 µg g<sup>-1</sup> and in

two cases and in association with non-compliance of Pb where total Cr exceeded 1000  $\mu\text{g g}^{-1}$ . Regarding the latter, the mass ratio of Cr:Pb of about 1:4 suggests that Cr in these samples exists as Cr(VI) in the form of the pigment,  $\text{PbCrO}_4$  (Turner and Solman, 2016), implying non-compliance in respect of both metals. Based on these observations, 12 out of 15 non-compliant (or potentially non-compliant) samples were selected for extraction tests, with three not considered where Cd concentrations were marginally above its RoHS threshold. These samples are illustrated in Figure 2 and characterised according to results from both FTIR and XRF analyses in Table 2.

### *3.2. PBET results and kinetic modelling*

The concentrations of elements extracted from ~100 mg of plastics in 40 ml of avian-PBET fluid and corrected for concentrations in the corresponding controls are shown as a function of time in Figure 3. In most cases, elemental concentrations increase in a biphasic fashion with relatively rapid initial mobilisation followed by a slower and more protracted period in which equilibrium appears to be approached or attained within the timeframe of the experiment. In the case of Br, initial mobilisation is evidently extremely rapid with equilibrium conditions not met by the end of the incubation, and with respect to Cr and, in three cases, Pb, there appears to be a period of relaxation (e.g. adsorption or precipitation) following initial mobilisation.

The timed PBET data were fitted using one of two kinetic models based on the diffusion-controlled and surface reaction-controlled dissolution of solids as outlined by Ruby et al. (1992) and Turner and Price (2008). Thus, a pseudo-first-order diffusion model, derived from a modified form of the Noyes-Whitney equation,

predicts that the rate of mobilisation is proportional to the magnitude of the concentration gradient around the particles, and whose solution is:

$$\ln(C_e - C) = \ln C_e - k_1 S t \quad (1a)$$

Here,  $C$  and  $C_e$  represent the observed (time-dependent) and equilibrium aqueous elemental concentrations, respectively,  $S$  is the surface area of undissolved solid, and  $k_1$  is a combined (forward and reverse) pseudo-first-order rate constant. In the case where the initial mobilisation is too rapid to be modelled, a constant,  $a$ , may be introduced that defines an effective starting concentration:

$$\ln(C_e - C) = \ln C_e - k_1 S t + \ln a \quad (1b)$$

An alternative, diffusion-controlled and parabolic model derived from Fick's second law for the dissolution of a semi-infinite slab is:

$$C = 2(C_e - C)(\sqrt{D/\pi})t^{1/2} = k_2 t_{1/2} \quad (2a)$$

where  $D$  is the diffusion coefficient of the aqueous element. Likewise, accounting for extremely rapid initial mobilisation, a constant,  $b$ , defining an effective starting concentration can be introduced:

$$C = 2(C_e - C)(\sqrt{D/\pi})t^{1/2} + b = k_2 t_{1/2} + b \quad (2b)$$

Models 1 and 2 were applied to the data in Figure 3 to determine which mechanism(s) and kinetics best describe metal mobilisation in the simulated avian proventriculus-gizzard. For model 1a, concentrations at equilibrium were defined as those measured at the end of the incubations and, for simplicity,  $S$  was assumed to be constant and was not factored into the calculations. The rate constant was derived from linear regression analysis of  $\ln(C_e - C) - \ln C_e$  versus  $t$ , forced through the origin, with the number of data points ( $n$ ) constrained to those whose concentrations were less than  $C_e$ . Model 1b was employed where regression analysis of  $\ln(C_e - C) - \ln C_e$  versus  $t$  and without forcing returned a significant y-intercept. For model 2, and given that  $D$  is a constant, both  $k_2$  and  $b$  were derived from the slope and intercept arising from linear regression analysis of  $C$  versus  $t_{1/2}$ .

The results, as rate constants, regression coefficients defining the linearised data and, for model 1,  $C_e$ , are shown in Table 3, while model fits using these values are annotated on Figure 3. Thus, for all elements with the exception of Br, model 1 provided the better fits, with only two cases (Ba in expanded polystyrene and Cd in a fragment of polyethylene) requiring an intercept to account for initial, rapid mobilisation. Model 2 successfully fitted Br data for two samples (expanded polyurethane and expanded polystyrene), requiring intercepts of more than 70% of the corresponding values of  $C_e$  in both cases. Also shown in Table 3 are maximum and equilibrium elemental bioaccessibilities ( $BA_{\max}$  and  $BA_e$ , respectively) for each time-course modelled. Bioaccessibilities, on a percentage basis, were calculated by converting the highest or final aqueous concentrations to a weight basis and normalising to the corresponding total (XRF) elemental concentrations.

### 3.3. *Implications for exposure to seabirds*

Regarding the two beaches sampled in the present study, the amount of RoHS non-compliant material retrieved on a number basis was about 8%. With the restrictions or phasing out of harmful additives in plastics, this percentage reflects the relative abundance of historical material washed up on the strandline and is, likely, representative of the more general plastic population suspended at sea where procellariiforms and other seabirds feed. Despite PVC being denser than sea water, its presence on the strandline suggests that small fragments may evade deposition while carried in the water column or be transported locally as bed-load. The fact that fragments of PVC have been observed in the digestive tracts of seabirds, including procellariiforms (Furtado et al., 2016), is consistent with the former assertion and may reflect the propensity of small particles to be suspended at the sea surface microlayer (Song et al., 2015) or the tendency of many pursuit plunging birds to feed well below the surface (Tavares et al., 2017).

The avian PBET results of this study predict various degrees of mobilisation of hazardous elements once non-compliant plastics have been ingested, with Br and Pb exhibiting the greatest concentrations in the simulated digestive fluid and yielding the highest bioaccessibilities on a percentage basis (and in excess of 10% and 20%, respectively, in one case each). Pseudo-first-order fits to most metal-metalloid data with rate constants on the order of  $0.05 \text{ h}^{-1}$  suggest that mobilisation may be constrained by the penetrability of the digestive fluid into the hydrophobic, non-porous plastics (Nakashima et al., 2016); as such, equilibrium is attained within the timeframe in which non-food material is trapped in the proventriculus-gizzard (weeks to months; Avery-Gomm et al., 2012). In some cases, where competing or transient

reactions are evident (e.g. Cr and Pb), mobilisation in the digestive tract may exceed equilibrium values within the first few days of ingestion, suggesting that accessibility would be greater should material be regurgitated and expelled during this period. In contrast, mobilisation of Br from the more porous expanded plastics appears to proceed continuously after an initial, extremely rapid period of mobilisation. Here, it is suspected that the substrate is modified or partially consumed at the onset of digestion with subsequent mobilisation of Br not constrained by fluid penetration. These observations suggest that significant release of brominated compounds is likely immediately after ingestion and that further release is dependent on the precise time of entrapment in the digestive tract rather than the hydrophobicity of the polymeric surface.

The significance of microplastics as a source of exposure to hazardous elements compared to exposure arising from the diet was evaluated using the results from the present study, an estimate for the fraction of plastic in ingested fulmar food of  $4.75 \times 10^{-5}$  (Herkze et al., 2017) and dry weight concentrations of elements reported for muscle tissue of Atlantic fish typical of the fulmar diet. With measurements for the latter restricted to Cd and Pb, and with respective median concentrations of about 0.01 and  $0.03 \mu\text{g g}^{-1}$  (Julshamn et al., 2013; Karl et al., 2016), fractional exposure arising from ingested plastics is predicted to be about 0.95 and 0.98, respectively, based on the highest elemental concentrations in beached materials reported in Table 2 (that is,  $4310 \mu\text{g g}^{-1}$  for Cd and  $38,200 \mu\text{g g}^{-1}$  for Pb). Using the maximum bioaccessible concentrations of Cd and Pb in plastics on a dry weight basis derived from the data in Table 3 ( $36.3 \mu\text{g g}^{-1}$  for Cd and  $928 \mu\text{g g}^{-1}$  for Pb), respective fractional exposures are reduced to around 0.15 and 0.6. Clearly, these figures are overestimates that require

selective ingestion of the most contaminated materials, and more realistic measures must account for the relative abundance of Cd- and Pb-positive items within the available plastic population. Thus, based on weighted average concentrations and a frequency of RoHS-non-compliance among the samples tested by XRF of about 4%, fractional exposures to the fulmar arising from plastic become about 0.007 and 0.06 for Cd and Pb, respectively.

Regarding Br, if it is assumed that the total concentration in plastic is equivalent to the combined concentrations of brominated flame retardants (BFRs) (Massos and Turner, 2017), calculations may be performed using available data on BFRs in Atlantic prey. Jenssen et al. (2007) report maximum, summed concentrations of various BFRs in cod lipid that are equivalent to whole body concentrations on a dry weight basis of about 1 ng g<sup>-1</sup>. Undertaking calculations as above yield a maximum fractional exposure to BFRs due to ingested plastic of 0.99, which is reduced to 0.90 when bioaccessibility is factored in and about 0.3 once the abundance of Br-positive plastics have been taken into account.

Assuming that hazardous chemicals in ingested prey are entirely accessible and that absorption across the intestinal epithelium is independent of the source or speciation once mobilised, ingested plastics are, on average, predicted to contribute about 0.7%, 6% and 30% to the respective net accumulations of Cd, Pb and Br (as BFRs) in the fulmar. The high contribution for the latter is qualitatively consistent with the relatively small size of BFR molecules and their greater propensity to migrate from the polymeric matrix than particulate, metallic additives (Hansen et al., 2013; Jang et al., 2016), and the accumulation of specific BFRs by procellariiforms that are present

in plastic but absent in prey (Tanaka et al., 2013). Thus, although ingested plastics appear to represent a negligible source of relatively high molecular weight hydrophobic organic pollutants to pelagic seabirds (Herkze et al., 2017), they may act as a significant vehicle for the accumulation of lower molecular weight BFRs and for metallic additives.

## Acknowledgements

Dr Andrew Fisher, Mr Chiu Ho and Mr Rupert Goddard (PU) are thanked for technical assistance and advice during the study. This work was funded in part by a PU Marine Institute HEIF V grant.

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462 *Sciences of the United States of America* 112, 11899-11904.

463 Table 1: Summary statistics for the elemental concentrations in 185 beached plastic samples along with the number of cases of RoHS non-compliance (or, for Br and Cr,  
 464 potential non-compliance).

	<b>As</b>	<b>Ba</b>	<b>Br</b>	<b>Cd</b>	<b>Cr</b>	<b>Hg</b>	<b>Pb</b>	<b>Sb</b>	<b>Se</b>
<i>n</i>	14	80	49	9	86	8	28	14	4
mean, $\mu\text{g g}^{-1}$	97.7	744	202	1270	201	35.3	2130	1270	568
median, $\mu\text{g g}^{-1}$	31.4	494	34.3	845	69.9	23.4	75.4	244	547
min, $\mu\text{g g}^{-1}$	7.3	118	6.0	57.0	18.3	8.3	2.6	37.4	319
max, $\mu\text{g g}^{-1}$	368	8680	2370	4310	1330	90.0	38200	15000	858
RoHS-non-compliance			3	7	2	0	5		

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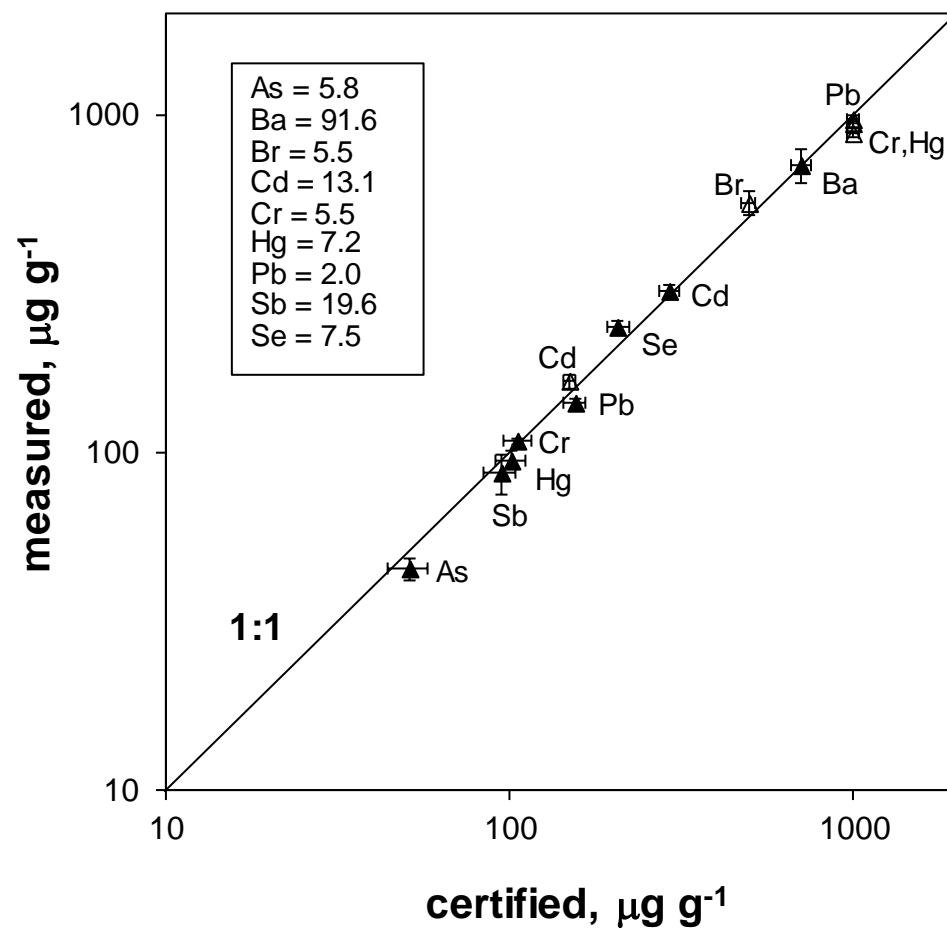
475 Table 2: Characteristics and elemental concentrations (in  $\mu\text{g g}^{-1}$ ) of the samples used in the extraction tests and as photographed in Figure 2. Note that As and Hg were not  
 476 detectable. (PE = polyethylene; PP = polypropylene; PVC = polyvinyl chloride; E-PS = expanded polystyrene; E-PU = expanded polyurethane.)

sample	thickness, mm	type	Ba	Br	Cd	Cr	Pb	Sb	Se
1	2.6	PP	246	3.2	1380				319
2	10.4	E-PU	188	2370		486			
3	2.1	PP	479			1090	4260	242	
4	2.9	PE	325		2060	18.4			469
5	1.6	PE	704		4310				858
6	1.7	PE			57.0	716	3680		
7	15.0	E-PS		1070		191			
8	21.7	E-PS	253	1750		199			
9	3.8	PP	737			1330	6130	247	
10	2.8	PVC		15.4			4090		
11	3.2	PP	515		2340				625
12	7.0	PVC	360	305			38200	108	

Table 3: Results of fitting models 1 or 2 to the data in Figure 3, along with equilibrium and maximum aqueous concentrations and bioaccessibilities (ns = results of regression analysis non-significant).

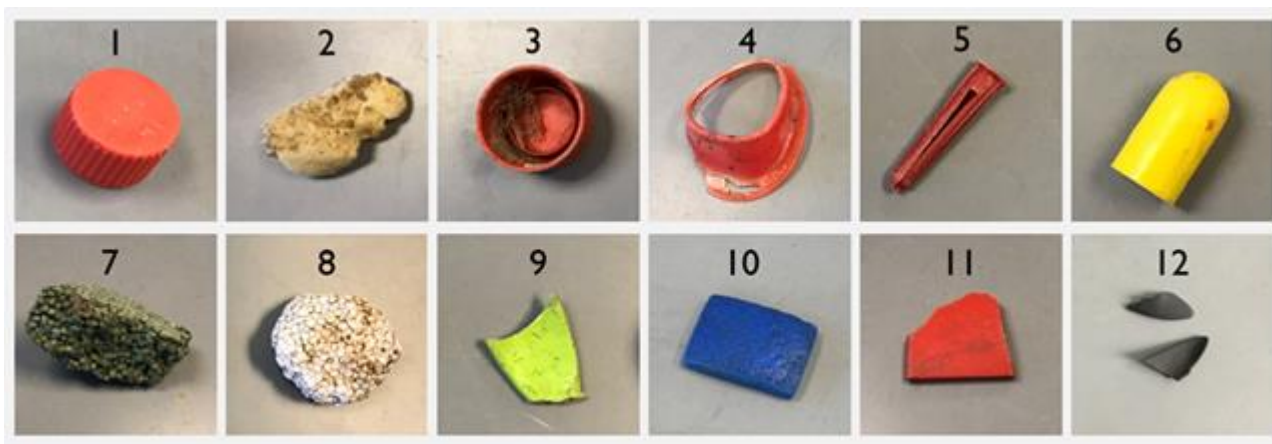
		1	2	3	4	5	6	8	9	10	11	12
Ba	$k_1, h^{-1}$	0.0426						0.0288	0.0562			
	$r^2 (n)$	0.996 (6)						0.916 (5)	0.982 (6)			
	$C_e, \mu g L^{-1}$	31.4						11.6	104			
	$a, \mu g L^{-1}$							5.0				
	$BA_e, \%$	5.11						1.83	5.64			
Br	$k_2, (\mu g L^{-1})^{-1} h^{-1}$		9.47					7.4				
	$r^2 (n)$		0.928 (7)					0.966 (7)				
	$C_e, \mu g L^{-1}$		412					471				
	$b, \mu g L^{-1}$		291					373				
	$BA_e, \%$		6.95					10.8				
Cd	$k_1, h^{-1}$	0.0614			0.0339	0.0326	0.0749				0.0444	
	$r^2 (n)$	0.956 (6)			0.907 (6)	0.954 (6)	0.880 (6)				0.993 (6)	
	$C_e, \mu g L^{-1}$	90.7			14.9	23.8	1.43				38.0	
	$a, \mu g L^{-1}$				6.0							
	$BA_e, \%$	2.63			0.29	0.22	1.00				0.65	
Cr	$k_1, h^{-1}$								0.558			
	$r^2 (n)$								0.899 (3)			
	$C_e, \mu g L^{-1}$								77.0			
	$C_{max}, \mu g L^{-1}$								81.9			
	$BA_e, \%$								2.32			
Pb	$k_1, h^{-1}$			0.297			0.282		0.0595	0.179		0.0387
	$r^2 (n)$			0.336 (3)			ns (3)		0.969 (6)	ns (3)		0.809 (6)
	$C_e, \mu g L^{-1}$			83.7			49.7		832	1640		3070
	$C_{max}, \mu g L^{-1}$			128			70.0			2320		
	$BA_e, \%$			0.79			0.54		5.43	16.04		3.21
Sb	$k_1, h^{-1}$			1.20			0.66			22.7		
	$r^2 (n)$			0.0538					0.0419			
	$C_e, \mu g L^{-1}$			0.982 (6)					0.995 (6)			
	$C_{max}, \mu g L^{-1}$			27.6					27.9			
	$BA_e, \%$			4.56					4.52			
Se	$k_1, h^{-1}$	0.0358			0.0243	0.0217					0.0631	
	$r^2 (n)$	0.818 (6)			0.935 (6)	0.737 (6)					0.719 (6)	
	$C_e, \mu g L^{-1}$	18.2			7.42	9.89					23.3	
	$BA_e, \%$	2.28			0.63	0.46					1.49	

483 Figure 1: Measured versus certified concentrations of elements in Niton polyethylene reference discs 1 ( $\Delta$ ) and 2 ( $\blacktriangle$ ). Errors represent two  
 484 standard deviations about the mean of 12 analyses (measured) and the 95% confidence interval for an unspecified number of measurements  
 485 (certified). Shown inset are indicative measurement limits of detection.





488 Figure 2: The primary and secondary plastics characterised in Table 2 and used to prepare the microplastics for the extraction tests.



498 Figure 3: Elemental concentrations extracted from ~100 mg of sample, and as coded in the Cr panel, by 40 ml of avian-PBET fluid. (Note that  
499 all elements evaded detection in sample 7.) Errors denote the standard deviation about the mean of three analyses and lines represent model fits  
500 according to equation 1 or equation 2 (Br only) using the coefficients given in Table 2.

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